

# Si (–Zr)/Ag multilayer thin-film anodes for microbatteries

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## Abstract

Thin film Si/Ag and (Si–Zr)/Ag multilayer electrodes are fabricated on a Cu substrate by alternate sputtering from Si (–Zr) and Ag at room temperature, and their electrochemical properties are investigated. The insertion of the Ag layer into the Si layer improves the cycling performance. The cyclability can be further improved by doping Zr into the Si layer of the Si/Ag multilayer thin films. The effects of the electrode configuration and the contact stability between the current-collecting layer and the electrode on the cycling performance are discussed.

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## 1. Introduction

A Li metal thin film has been usually used as a negative electrode of a microbattery to power microdevices, in which all the battery components are formed in the shape of solid-state thin films [1]. However, its low melting point and strong reactivity with moisture limit applications and fabrication processes. So, an alternative thin-film negative electrode with better thermal and chemical stability is required, and several materials have been reported [2–4]. Si is a very attractive candidate for the negative electrode, because it reacts with 4.4 moles of Li per a mole, and it can show little irreversible capacity at the initial cycle [5].

Recently, it has been reported that Si thin-film electrodes prepared by a sputtering method, showed poor cycle performance due to large volume change and subsequent electrode cracking [6]. On the other hand, SiAg powders prepared by mechanical alloying method, containing a uniform dispersion of Si in ductile Ag, could be a good choice as a negative electrode material for Li-ion battery [7].

To improve the cycle performance of Si thin film electrode we designed a Si/Ag multilayer thin film electrode, which is a nano-scaled composite perpendicular to the substrate. Ag is chosen as a separating layer for some reasons as follows.

1. Ag is ductile to relieve the stress due to the volume expansion of Si.

2. Ag is mixed conducting material for Li ion and electron.
3. Ag is immiscible with Si, which leads to large reversible capacity and electrode stability at the elevated temperature in the packaging process of a microbattery-embedded device.

In this study, we fabricated Si/Ag multilayer thin-film electrode, and investigated their electrochemical characteristics.

## 2. Experimental

Multilayer Si/Ag and (Si–Zr)/Ag thin films were fabricated on Cu substrate (12 mm diameter) by depositing Si and Ag or Si–Zr and Ag, by turns, respectively, using magnetron sputtering at room temperature. The Si–Zr layer was deposited by co-sputtering of two separate targets, Si and Zr. The alloy composition and thickness of the layer were controlled by the rf power for each target and deposition time, respectively. For some Si/Ag thin film electrodes vanadium thin film (5 nm thickness) was pre-deposited on Cu substrates. The base pressure was under  $2 \times 10^{-6}$  Torr and the working pressure was  $5 \times 10^{-3}$  Torr in the Ar atmosphere. The sample specifications are given in Table 1. The thickness of each layer was monitored during the deposition by a quartz-crystal thickness monitor.

For electrochemical measurements, coin-type test cells were constructed using the film electrodes in 2016 coin cell hardware. The cells used a separator, an electrolyte (1 M LiPF<sub>6</sub> dissolved in a 50:50 vol.% mixture of ethylene

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Table 1  
The specifications of the Si/Ag and (Si–Zr)/Ag multiplayer thin film electrodes

Sample name	Si (–Zr)			Ag (top layer)			Electrode thickness (Å)	Stacking <sup>a</sup>
	Number of layers	Layer thickness (Å)	Total thickness (Å)	Number of layers	Layer thickness (Å)	Total thickness (Å)		
A	2	575	1150	1	50	50	1200	S/A/S
B	3	467	1400	2	50	100	1500	S/A/S/A/S
C	4	340	1360	3	50	150	1510	S/A/S/A/S/A/S
D	8	179	1435	7	50	350	1785	S/A/S/A/S/A/S/A/S/A/S
E	8	166.5	1332	7	100	700	2032	S/A/S/A/S/A/S/A/S/A/S/A/S/A/S
F	5	150	751	4	50	200	951	S/A/S/A/S/A/S/A/S
G	4	155	620	3	70	210	830	S/A/S/A/S/A/S
H	4	155	620	3 (1)	70 (35)	245	865	S/A/S/A/S/A/S/A
I	4	155	620	3	70	210	830	V/S/A/S/A/S/A/S
J	4	225	900	3	50	150	1050	SZ/A/SZ/A/SZ/A/SZ

<sup>a</sup> In stacking sequence, A, S, SZ and V represent Ag, Si, Si–Zr and V, respectively.

carbonate (EC) and diethyl carbonate (DEC)) (provided by Cheil Industries Inc., Korea), and lithium foils for the counter and reference electrodes. Cells were assembled and crimped closed in an argon-filled glove box. All cells were tested at 30 °C with a constant current of 30  $\mu$ A between 0.15 and 1.5 V.

The composition analysis for the Si–Zr layer was carried out by Rutherford backscattering spectroscopy (RBS).

### 3. Results and discussion

Fig. 1 shows charge–discharge curves of the Si/Ag electrode (sample D) between 0.15 and 1.5 V for the first two cycles. The differential capacity versus voltage at the first and second cycles for sample D, pure Si and Ag-top-layered Si/Ag (sample H) electrodes are shown in Fig. 2a–c, respectively.

The differential capacity curves of sample D (Fig. 2a) and Si thin-film electrode (Fig. 2b) are very similar. Any distinct

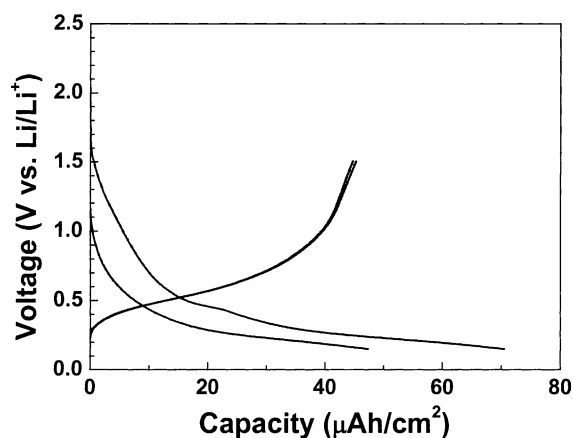


Fig. 1. The first and second discharge–charge curves for the sample D.

change induced by the insertion of the Ag layers is not observed. According to the recent study on the microstructure of Si/Ag multilayer films prepared by using ion-beam sputter deposition technique [8], an amorphous Si layer and a polycrystalline Ag layer form a sharp and continuous interface without any diffused and reacted region due to their uphill diffusion attributed to their immiscibility between Si and Ag. Hence, if the thickness of the Ag layer is thin enough and the Li diffusion through the Ag layer is fast enough, that the overall electrochemical reaction of Si/Ag multilayer and Si thin film electrode during cycling appear to be almost identical. The substantial Li insertion into Ag occurs below 0.07 V [7].

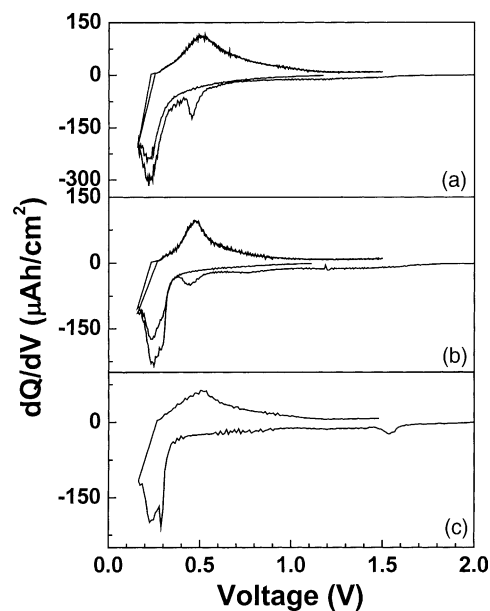


Fig. 2. The differential capacity vs. voltage for the first and second cycle of the Si and Si/Ag multiplayer thin film electrodes: (a) sample D; (b) Si; (c) sample H.

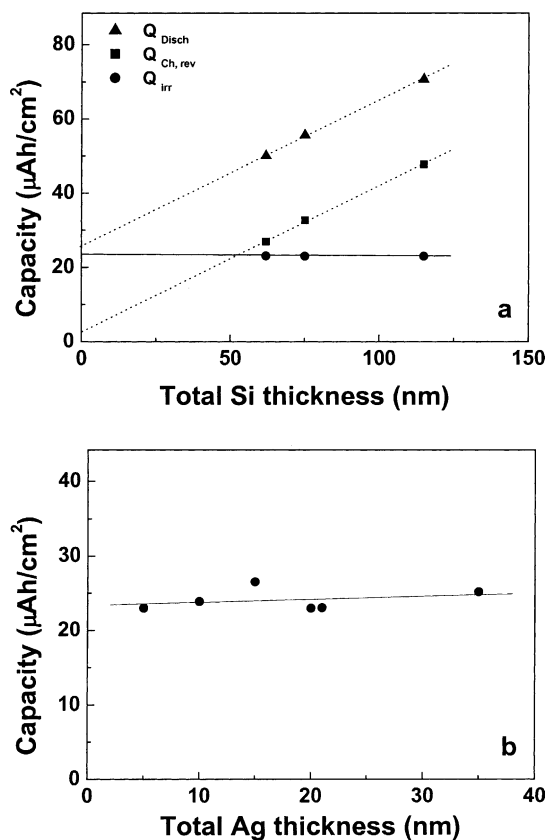


Fig. 3. The reversible and irreversible capacity at the first cycle as a function of the total thickness of (a) Si layers and (b) Ag layers in the Si/Ag multiplayer thin film electrodes.

The first reduction peak observed around 0.45 V observed at the first cycle disappears at the second cycle for sample D and Si thin film electrode. By contrast, Si/Ag thin film electrode covered with Ag layer on the surface, sample H, does not show this peak. This suggests that the irreversible reaction at around 0.45 V seems to be related to an interfacial reaction between Si surface and liquid electrolyte.

There is a considerable amount of irreversible capacity between the first discharge (Li insertion process) and the charge (Li extraction) as shown in Fig. 1. The first discharge and charge capacity, and the initial irreversible capacity loss for various Si/Ag multilayer thin film electrodes are plotted as the function of total Si and Ag thickness in the Fig. 3a and b, respectively. In Fig. 3a, the first discharge capacity and the first charge capacity increase in proportion to the total active Si thickness. The irreversible capacity loss is not dependent on the total Si and Ag thickness in multilayer films. This suggests that the irreversible capacity observed in the Si/Ag thin film electrodes, is not due to intrinsic bulk characteristics, but mainly related with the interfacial reaction between the electrode surface and the liquid electrolyte. Fig. 4 shows the cycle performances of the Si/Ag multilayer thin film electrodes. The cyclability improves when the number of layers increases and the thickness of the Si layer is decreases, as inferred from the comparison of samples, A,

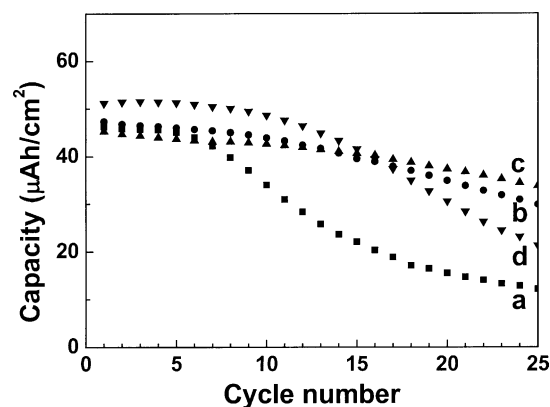


Fig. 4. The capacity vs. cycle number for the Si/Ag multiplayer thin film electrodes: (a) sample A; (b) sample C; (c) sample D; (d) sample E.

C and D. This indicates that the inserted Ag layer enhances the cyclability, it is likely that the ductile Ag layer relieves the stress in the Si layer during cycling. On the other hand, the comparison of samples D and E depicts that increasing the thickness of the Ag layer, adversely affects the cyclability. When the thickness of the Ag layer is too thick, Li can be irreversibly trapped in the Ag layer, which consequently makes the electrode kinetically unfavorable. Therefore, it is important to control the number of layers, and thickness of Si and Ag layer to optimize the electrode property.

For lithium storage metals such as Sn and Si, the drawback due to the large volume change during cycling could be overcome by alloying the active and inactive elements [9,10]. A strong affinity between components of silicide alloys seems to be essential for good cyclability of silicide electrodes [11]. The Zr–Si system was chosen here, because of its large negative heat of mixing of the constituent elements. The composition of the Si–Zr layer is  $\text{Si}_{0.8}\text{Zr}_{0.2}$ , and the structure of the Si–Zr layer determined by XRD is amorphous or nanocrystalline alloy, because no peak is observed (data not shown here). As expected, Zr-doping into the Si layer of the Si/Ag multilayer thin film electrode appears to be a good strategy to improve the cycling performance as shown in Fig. 5.

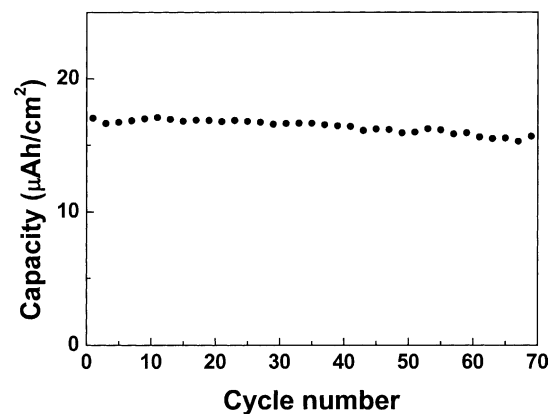


Fig. 5. The capacity vs. cycle number for the  $(\text{Si}_{0.8}\text{Zr}_{0.2})/\text{Ag}$  multilayer thin film electrode (sample J).

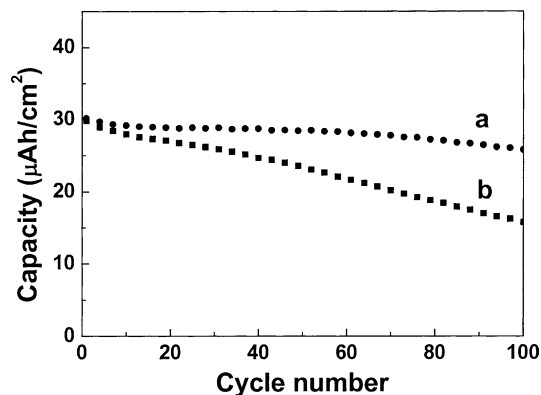


Fig. 6. The capacity vs. cycle number for the Si/Ag multilayer thin film electrodes (a) with (sample I) and (b) without a V intermediate layer (sample G).

On the other hand, as microbatteries have several solid/solid contacts, the stability at the interface during operation may affect battery performances. To improve the stability of electrode/substrate interface, through enhanced adhesion and buffering, a vanadium (V) layer is inserted between a Cu current collecting substrate and a Si/Ag multilayer thin film electrode. V is chosen because of its excellent toughness. The V intermediate layer leads to a distinct improvement of cyclability for the Si/Ag multilayer thin film electrode as shown in Fig. 6.

#### 4. Conclusions

It has been shown that by designing a multilayered structure of Si/Ag thin films instead of single-phase Si, the cycling stability of Si thin film can be improved significantly.

It appears that the cyclability can be further improved by doping Zr into the Si layer of the Si/Ag multilayer thin film. A Si/Ag or a (Si–Zr)/Ag multilayer thin film is promising as a negative electrode for rechargeable thin film microbattery.

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